

## REMOVAL OF HYDROGEN CHLORIDE FROM HIGH TEMPERATURE COAL GASES

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### Introduction

The chlorine content of U.S. coals ranges from 0.01 to 0.5%, and some coals in U.K. contain as high as 1.0% chlorine.<sup>1</sup> This element is present in the coal mainly as alkali chlorides, but it also occurs as oxychlorides of calcium and magnesium.<sup>2</sup> During coal gasification or combustion, these chloride species are converted to HCl vapor. Concentrations of HCl vapor in coal gas have been found in the range 1 to 500 ppm.<sup>3</sup> The presence of HCl in the coal gas can lead to corrosion of metallic and ceramic components of the gasifier, attack gas turbine components and to poisoning of molten carbonate fuel cell electrodes.

Morgantown Energy Technology Center, as the U.S. Department of Energy's lead center for coal gasification and gas stream cleanup technology, has been concerned for some years with the purification of coal-derived gases for a range of applications including gas turbine, fuel-cell, and combined-cycle power generation. Removal of harmful impurities from the coal gas stream at elevated temperatures (>500°C) is necessary for achieving high thermal efficiency in such applications. Although the tolerance to HCl level of fuel cells has not been determined accurately, it is typical to specify that fuel cell feedstocks should contain no more than 1 ppm HCl. Similar requirements may be necessary in turbine applications. Currently available processes for removing HCl vapor operate at relatively low temperatures ( $T < 300^\circ\text{C}$ ) and thus they are not suitable for use with hot coal gases ( $T > 500^\circ\text{C}$ ). This paper presents the results of a laboratory-scale evaluation conducted at SRI International to determine the effectiveness of naturally occurring minerals and commercially available sorbents to remove HCl vapor from simulated coal gas streams at temperatures from 550° to 650°C.<sup>4</sup>

The thermodynamic stability and the volatility of the solid chloride products were the major criteria in selecting the nature of the sorbent. Alkaline earth chlorides, generally, are less volatile than alkali metal chlorides and transition metal

chlorides. However, the calculated equilibrium partial pressure of HCl over alkali metal chlorides were calculated to be lower than those over alkaline earth compounds (Table 1). In considering these two factors, along with availability in a natural form, sodium carbonate based sorbents were judged to be superior to other compounds.

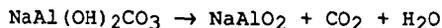
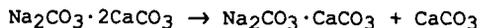
Table 1

EQUILIBRIUM PARTIAL PRESSURES OF HCl AND METAL CHLORIDES  
AT 900 K IN PRESENCE OF A SIMULATED COAL GAS

Parent Compound	Product chloride (MCl)	Equilibrium Partial Pressure (atm)	
		HCl	MCl
Na <sub>2</sub> CO <sub>3</sub>	NaCl	1.5 x 10 <sup>-6</sup>	3.5 x 10 <sup>-6</sup>
K <sub>2</sub> CO <sub>3</sub>	KCl	3.0 x 10 <sup>-6</sup>	8.0 x 10 <sup>-6</sup>
BaCO <sub>3</sub>	BaCl <sub>2</sub>	2.2 x 10 <sup>-5</sup>	1.5 x 10 <sup>-11</sup>
CaCO <sub>3</sub>	CaCl <sub>2</sub>	9.5 x 10 <sup>-4</sup>	2.8 x 10 <sup>-9</sup>
SrCO <sub>3</sub>	SrCl <sub>2</sub>	1.5 x 10 <sup>-4</sup>	2.2 x 10 <sup>-11</sup>

Materials, Apparatus, and Experimental Procedures

Three naturally occurring minerals and a commercially available sorbent were selected for evaluation. The tested minerals were nahcolite (NaHCO<sub>3</sub>), shortite (Na<sub>2</sub>CO<sub>3</sub>·2CaCO<sub>3</sub>), and dawsonite (NaAl(OH)<sub>2</sub>CO<sub>3</sub>). The mineral samples were pelletized and calcined at 600°C. During calcination the minerals decomposed as follows:



The natural minerals are characterized by low specific surface areas and high levels of active sodium components (Table 2). The commercial sorbent was Katalco Chloride Guard 59-3, manufactured by Katalco Corporation, Oakbrook, IL. This product is sold to remove chloride vapor from natural gas and light hydrocarbon feedstocks. The sorbent contains a proprietary active sodium compound impregnated on a porous alumina support and shows a very high specific surface area with a low level of active sodium component.

Table 2  
 PROPERTIES OF SORBENTS

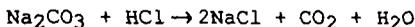
Sorbent	Bulk density (g.cm <sup>-3</sup> )	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	ASC <sup>1</sup> (wt% Na)
Katalco Chloride Guard 59-3	0.76	247.0	4.7
Shortite	1.46	0.25	15.0
Nahcolite	0.65	1.2	40.3
Dawsonite	0.59	2.3	16.5

<sup>1</sup>ASC = Active sodium component expressed as wt% sodium.

The reactivities of the selected sorbents toward HCl vapor were evaluated in a thin bed, microreactor (Figure 1) under isothermal conditions. A simulated coal gas of composition 22% H<sub>2</sub>, 34% CO, 7% CO<sub>2</sub>, 36% H<sub>2</sub>O, 1% He and 300 ppm HCl was used as a feedstock. The gas mixture was prepared by metering and blending the individual components using mass flow controllers. Glass or PTFE tubing was used to minimize adsorption or interaction of HCl vapor on the tube walls. Glass walls exposed to the HCl stream containing steam was kept heated to 180°C. The gaseous effluent leaving the sorbent bed was analyzed for HCl by reacting it with a 0.5 M NaHCO<sub>3</sub> buffer solution and measuring the dissolved [Cl<sup>-</sup>] with a chloride ion selective electrode. The cumulative concentration of the [Cl<sup>-</sup>] was calculated using the Nernst equation and the instantaneous partial pressure of HCl vapor in the reactor effluent was calculated by differentiating the cumulative chloride concentration with respect to time.

### Results and Discussion

The reaction of the sorbent with HCl vapor yielded solid NaCl as the product:



The rate of reaction with the sorbents was rapid initially, but it decreased with time onstream. Even at a space velocity of  $5 \times 10^4$  h<sup>-1</sup>, initial residual HCl vapor levels of about 1 ppm were attained with all the tested sorbents (Figure 2). The rate of removal of HCl and the chloride uptake capacity of the sorbents were found to be functions of the level of its active sodium component (ASC) and its surface area (Table 3). Calcined nahcolite and dawsonite, with their high ASCs and moderate surface

Table 3

## CHLORIDE UPTAKE CAPACITIES OF THE TESTED SORBENTS

Sorbent	Chloride capacity (wt%)	
	525°C	650°C
Katalco Chloride Guard	7.1	4.3
Shortite	4.4	4.6
Nahcolite	52.5	52.5
Dawsonite	21.9	18.0

areas had high chloride uptake capacities. The chloride capacity of shortite was the smallest of the sorbents tested because of its low surface area in spite of its high ASC level. The capacity of Katalco Chloride Guard 59-3 was limited by the ASC level, although its surface area was very high.

In the range of 525° to 650°C, the temperature had only a small effect on the rate of HCl removal by shortite and nahcolite. Similarly, their maximum chloride uptake capacities were not affected by temperature. However, for Katalco Chloride Guard and dawsonite the uptake capacity at 650°C was less than at 530°C. Since these sorbents contain alumina, it is likely that at 650°C, the interaction of the active sodium component with the alumina present in the sorbent decreased their reactivity with HCl vapor.

Under the experimental conditions used, with very high surface area sorbents such as Katalco Chloride Guard, the rate of chloride uptake was controlled initially by gas phase mass transfer. Mass transfer calculations indicated that the rate of HCl vapor transfer from the gas phase (300 ppm) to the surface of Katalco Chloride Guard sorbent at 525°C would be about  $2 \times 10^{-6}$  mole·g<sup>-1</sup>·s<sup>-1</sup> which compared favorably with the measured initial rate of  $1 \times 10^{-6}$  mole·g<sup>-1</sup>·s<sup>-1</sup> at that temperature. At longer exposures, the rate became limited by pore diffusion. Effectiveness factor calculations indicated that pore diffusion could control the rate of chloride uptake with Katalco Chloride Guard once the external areas have been reacted. This rate limitation was confirmed when larger particles were found to react more slowly than smaller particles<sup>4</sup> in the size range of 0.05 to 0.5 cm. Rate control by other mechanisms such as chemical reaction at the interface or diffusion through the chloride product layer became predominant only when the sorbent was nearly saturated.

To determine the rate control mechanism with moderate surface area sorbents such as nahcolite, small quantities (0.1 g) of nahcolite were exposed to the gas mixture at a space velocity of  $1 \times 10^5 \text{ h}^{-1}$  for various periods of time and the accumulated chloride in the solid was measured. Because of the small quantity of the sorbent and the large flow rate, the concentration of HCl vapor and the composition of the sorbent across the bed could be assumed to be nearly constant. The results of these experiments indicated that the rate of HCl reaction with nahcolite was limited initially by mass transfer. However, beyond an initial period, chemical reaction at the interface controlled the rate through a major portion of the sorbent active life time as indicated by a linear correlation between the log of the unreacted fraction (1-x) of the sorbent and time (Figure 3). This behavior is to be expected because of the relatively fewer number of micropores in a moderate surface area material in comparison with a high surface area material. Hence, the shift from mass transfer limited rate to chemical reaction limited rate would occur earlier with nahcolite than with Katalco Chloride Guard. After about 80% of the nahcolite sorbent has been reacted, the rate control appears to be limited by diffusion through a chloride product layer as indicated by the non linear behavior in log (1-x) vs. time plot.

Bench-scale experiments were also conducted with these sorbents at the Institute of Gas Technology, Chicago, IL.<sup>5</sup> The rate of chloride uptake was calculated from the analysis of the chloride content of the spent sorbent as a function of the bed depth. The results of bench-scale experiments were in general agreement with the laboratory-scale experiments although the HCl removal rate and the chloride capacities were somewhat lower than found in the laboratory-scale experiments. This may be due to the large particles used in the bench-scale study. Impurities such as H<sub>2</sub>S and trace metals did not affect significantly the rate of HCl removal or the chloride capacities of the sorbents.

A preliminary economic analysis was performed at SRI to determine the cost of HCl removal from hot coal gas.<sup>4</sup> The cost of using Katalco Chloride Guard was estimated to be too high (~\$0.02/kWh) for use as throwaway sorbent. In contrast, the annual operating cost for the use of nahcolite was estimated to vary from \$0.0017 to \$0.0031/kWh depending on whether the gasifier is oxygen-blown or air-blown. In this annual operating cost, the capital investment and the capital recovery components are major cost factors whereas the cost of nahcolite sorbent and its chloride capacity have only a small impact.

### Conclusions

The reaction of HCl vapor with calcined sodium-carbonate based natural minerals and synthetic sorbents is rapid and the HCl vapor

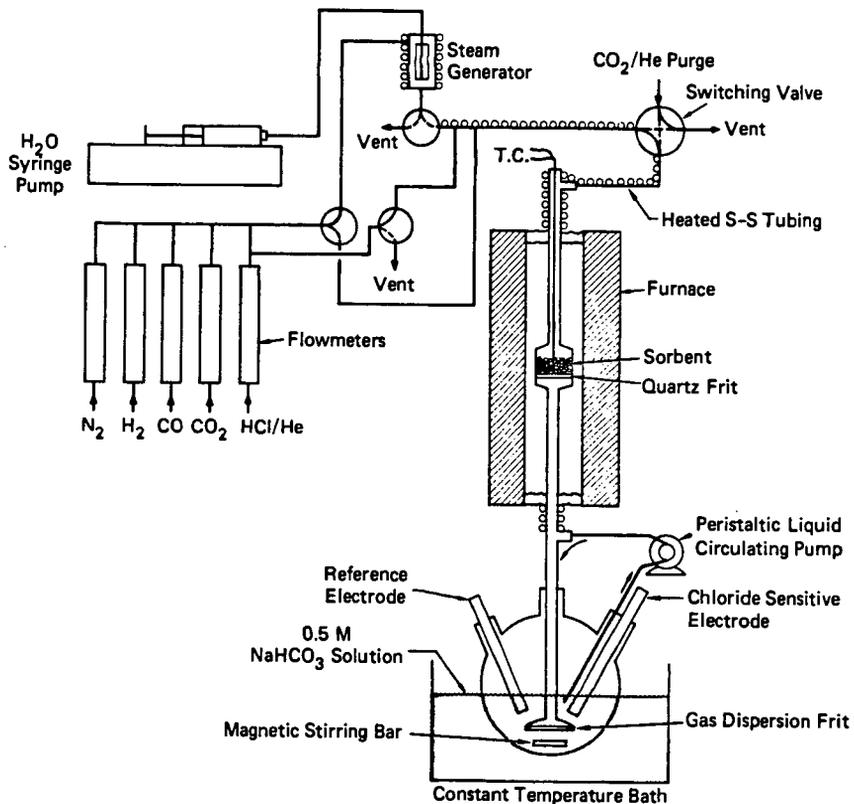
concentration can be reduced to about 1 ppm level in coal gas in the temperature range of 525° to 650°C. The rate of reaction is controlled initially by the rate of mass transfer from the gas phase to the surface of the sorbents. At later times the rate is controlled by diffusion through micropores in high surface area sorbents and by chemical reaction in moderate and low surface area sorbents. The presence of H<sub>2</sub>S and trace metal impurities did not affect significantly the performance of the sorbents. The cost of HCl removal using naturally occurring mineral, nahcolite, is very low.

#### Acknowledgment

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Figure 1. Schematic diagram of thin bed reactor for studying HCl removal.

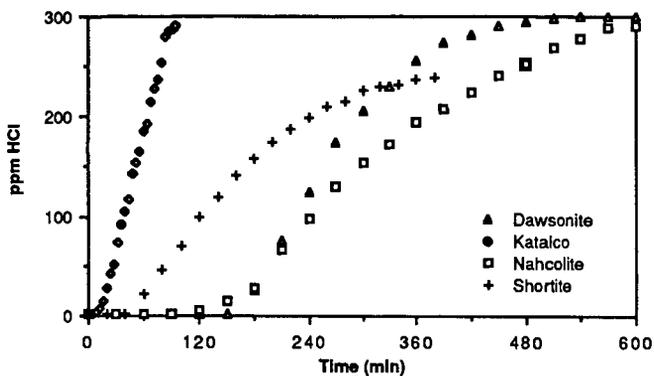


Figure 2. Examples of HCl Breakthrough Curves for Various Sorbents at 525°C  
 Sorbent quantity - Dawsonite = 0.4 g; Nahcolite = 0.2 g  
 - Katalco = 0.23 g; Shortite = 1.0 g

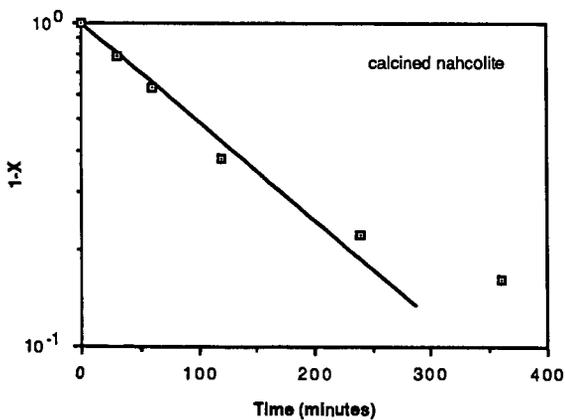


Figure 3 Plot of logarithm of unreacted fraction with time